References

1. MUTHUKUMAR, M., SEBASTIAN, K. & PANDIAN, S. J., *J. molec. Structure*, **27** (1975), 117.
2. WATERS, D. N., SHORT, E. L., THARWAT, M. & MORRIS, D. F. C., *J. molec. Structure*, **17** (1973), 389.
3. SANYAL, N. K., GOEL, R. K. & PANDEY, A. N., *Indian J. Phys.*, **49** (1975), 546.
4. CYVIN, S. J., *Molecular vibrations and mean square amplitudes* (Elsevier, Amsterdam), 1968.
5. WILSON, (Jr) E. B., DECIUS, J. C. & CROSS, P. C., *Molecular vibrations* (McGraw-Hill, New York), 1955.

Crystal Data on 12-Heteropoly Nioboantimonate

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A new heteropoly complex, 12-heteropoly nioboantimonate $K_{11}[SbNb_{12}O_{38}]14H_2O$ has been prepared and the X-ray crystal data recorded.

ONLY a few heteropoly compounds of niobium have been reported[1] in the literature. The present note deals with the preparation, characterization and X-ray crystal diffraction data of a new heteropoly complex, 12-heteropoly nioboantimonate, containing antimony as the hetero atom.

Aqueous solutions of potassium pyroantimonate and freshly prepared[2] potassium hexaniobate, $K_7Nb_6O_{19}.13H_2O$, were taken in the molar ratio 1: 12, refluxed for 4 hr. After leaving the solution under ambient conditions for three days it was kept *in vacuo* when small needle-shaped crystals separated out which were recrystallized from hot water. Analysis for potassium, niobium and antimony in the compound gave values 17·12, 44·58, 4·86% respectively as against the theoretical calculated values of 17·20, 44·59, 4·87% respectively. The percentage of water and oxygen, calculated by difference, came to 37·44. The individual estimation of hydrogen content in the compound came to 1·12% and hence the percentage of water was 10·02. Thus from these analytical percentage composition data, the compound has been finally represented as $K_{11}[SbNb_{12}O_{38}]14H_2O$, according to the views[3] suggested by Lindqvist.

From rotation and Weissenberg X-ray crystal diffraction studies, the cell parameters were found to be: $a = 14{\cdot}42$, $b = 22{\cdot}11$, $c = 11{\cdot}27$ Å and $\alpha = \beta = \gamma = 90$. The system is orthorhombic. The volume V per unit cell was calculated to be 3593·171 Å^3. The space group was uniquely established to be $I4_1/a$, from the systematic presence of reflections: hkl with $h+k+l = 2n$, ool with $l = 4n$ and hkl with $2k+l = 2n+1$ or $4n$. The last condition gives the number (n) of molecules per unit cell to be 4. The observed density, $\rho_{obs} = 4{\cdot}61$ g litre^{-1}. From the relation $\rho_{obs} = 1{\cdot}66\ M.n/V$, the molecular weight ($M$) of the compound came to 2494, against the theoretical value 2499·66.

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References

1. DALE, W. B., BUCKLEY, JANET M. & POPE, M. T., *J. chem. Soc.*, **2A** (1963), 301.
2. MILLER, G. L., *Metallurgy of the rare earth metals*, Vol. VI (Butterworths, London), 1959, 68.
3. LINDQVIST, I., *Chem. Abstr.*, **47** (1953), 728a; **48** (1954), 9782i.

Heats of Formation of Solid Solutions of CsCl with CsBr

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Substitutional impurity model of Dick and Das [*Phys. Rev.*, 127 (1962), 1053] has been extended to CsCl structure. A statistical treatment has been employed to calculate the heats of formation of solid solutions of $CsCl_{1-x}Br_x$ system. The results are in good agreement with experimental data; discrepancies occur only at high impurity ion concentrations.

FOR substitutional impurities in alkali halides which do not require charge compensation, relaxations in the defect crystal are essentially due to differences in the non-coulombic interaction terms. Studies of substitutional defects in alkali halide crystals employing the Born-Mayer model of ionic solids[1-6] have shown that the calculated heats of formation, ΔH_f^{ss}, are not entirely satisfactory in the initial composition range of solid solutions. Fancher and Barsch[4] have, however, shown that a statistical approach which includes relaxations of ions around impurities in accordance with the model of Dick and Das[1] yields good agreement between theoretical and experimental estimates of heats of formation in the entire range of the solid solutions formed by most of the alkali halides with the NaCl ($Fm3m$) structure (6:6 coordination). Cesium halides which possess the CsCl ($Pm3m$) structure (8:8 coordination) have not been subjected to much theoretical analysis. With our recent success on the calculation of energies of formation[5] and migration[6] of defects in these solids, we considered it worth while to employ the Born parameters to estimate the heats of formation of solid solutions of the $CsCl_{1-x}Br$ system which retains the CsCl structure throughout the composition range. Experimental heats of formation of solid solutions of $CsCl_{1-x}Br_x$ system are available in the literature[7].

Method of calculation — We have extended the single substitutional defect model of Dick and Das[1] to the CsCl structure, the details of which are given in the literature[1,4]. We have allowed four shells of ions to relax in this lattice as shown in Fig. 1.

The $\vec{\xi}_i$ ($i = 1, 2, 3, 4$) represent the displacements of the ions in terms of a, the lattice parameter of the crystal. The displacements $\vec{\xi}_i$ and the electronic dipole moment vectors $\vec{\mu}_i$ (in units of ea) of these polarized ions are assumed to be radially directed. The rest of the lattice is assumed to be undisplaced